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Fluorine-containing resin film-coated steel plate production - comprises  
coating steel plate with primer of mixed resin, preheating plate,  
applying copolymer, irradiating and heating

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Abstract (Basic): JP 9156036 A

Manufacture of a fluorine-contained resin film coated steel plate  
comprises (1) coating a steel plate with (A) primer composed of mixed  
resin of fluororesin and heat resistant resin, (2) preheating the  
plate, (3) applying (B) ethylene tetrafluoride perfluoroalkyl vinyl  
ether copolymer film to the plate, (3) irradiating the laminated plate  
with electron beams having the dosage of 5-50kGy from above the film  
(B) and (4) treating the plate at at least 320 deg. C.

USE - The obtained plate is used in cooking utensils.

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(54) Title of the Invention: A METHOD FOR MANUFACTURING A  
STEEL PLATE COATED WITH A FLUORINE-CONTAINING RESIN

(57) Abstract:

[Object] To obtain a resin-coated steel plate exhibiting both excellent heat resistant adhesive properties and excellent heat resistant non-stick properties, and suitable for use in cookware and heat-cooking utensils.

[Constitution] A method comprising coating the surface of the steel plate with a primer which consists of a mixture of a fluororesin and a heat resistant resin, baking the

coating, preheating the steel plate, laminating a layer of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film by press-adhesion, irradiating the resin film surface with electron beams at a dose of 550 kGy, and heating the steel plate at a temperature of 320 or higher.

[Claims]

[Claim 1] A method for manufacturing a steel plate coated with a fluorine-containing resin comprising coating the surface of the steel plate with a primer which consists of a mixture of a fluororesin and a heat resistant resin, baking the coating, preheating the steel plate, laminating a layer of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film by press-adhesion, irradiating the resin film surface with electron beams at a dose of 5-50 kGy, and heating the steel plate at a temperature of 320 or higher.

[Detailed Description of the Invention]

[Industrial Application of the Invention]

The present invention relates to a method for manufacturing a fluororesin film coated steel plate which is suitable for use in kitchen utensils such as cookware, heat-cooking utensils, and the like.

[Prior Art]

Fluororesin is widely used as a composite material with steel in food cooking utensils such as a bread or cake cooker (waffle iron), frying pan, heat-cooking utensils such as a microwave oven, an iron pot of jars, a gas table plate, and the like due to its superior heat resistance, non-stick properties, resistance to stain, and the like. Conventionally, fluororesin films are formed on food cooking utensils by coating a fluororesin or a mixture of a fluororesin and a heat resistant resin onto a steel plate surface and baking the coating at a high temperature.

However, because the coating is formed by baking a fluorine-containing paint, it is difficult to avoid formation of pinholes during the coating step and baking step. Because of this, non-stick properties and resistance to stain cannot be maintained over a long period of time. In addition, various defects may be produced through pinholes.

Formation of pinholes can be prevented by covering the surface of a steel plate with a fluororesin film with no holes. For example, Japanese Patent Applications Laid-open No. 124081/1978 and No. 98372/1978 disclose a method of causing a fluororesin film with no holes to adhere by laminating a film of fluorine-containing polymer heated to a temperature above the melting point of the fluorine-containing polymer over the steel plate surface and pressing the laminate with a rubber roller. Japanese Patent Application Laid-open No. 162243/1993 discloses a method of attaching a thermoplastic fluororesin film onto a steel plate surface by fusion via a surface-treated layer of a mixture of a fluororesin and a heat resistant resin. Moreover, Japanese Patent Applications Laid-open No. 344505/1994 and No. 125136/1995 disclose a method of improving adhesion properties of a fluororesin film by adjusting the temperature conditions of a heating and reheating treatment.

#### [Problems to be Solved by the Invention]

However, it is difficult to obtain a fluororesin

film coated steel plate which satisfies both heat resistant adhesive properties and heat resistant non-stick properties at the same time by using the conventional manufacturing conditions. Particularly, superior food burning resistant properties are required for the application to cookware or food heating utensils. However, sufficient food burning resistant properties cannot be obtained using conventional fluororesin film coated steel plates.

The present invention has been achieved to solve these problems and has an object of providing a fluorine-containing resin film coating with improved anti-food burning properties by irradiating electron beams onto the fluorine-containing resin film coating adhering to a steel plate from the film surface side.

[Means for Solving the Problems]

The above object can be achieved in the present invention by a method for manufacturing a steel plate coated with a fluorine-containing resin which comprises coating the surface of the steel plate with a primer which consists of a mixture of a fluororesin and a heat resistant resin, baking the coating, preheating the steel plate, laminating a layer of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film by press-adhesion, irradiating the resin film surface with electron beams at a dose of 550 kGy, and heating the steel plate at a temperature of 320 or higher. The steel plate used includes 55% Al-Zn alloy-plated steel plates, Al-plated steel plates, stainless

steel plates, and the like which may be optionally subjected to a phosphate treatment or a coating-type chromate treatment in advance.

A primer consisting of a mixture of a fluororesin and a heat resistant resin is applied to the steel plate and baked prior to press-adhesion and lamination of the tetrafluoroethylene perfluoroalkyl vinyl ether copolymer.

As the fluororesin which is a component of the primer, at least one resin selected from the group consisting of a polytetrafluoroethylene resin, tetrafluoroethylene perfluoroalkyl vinyl ether copolymer resin, and tetrafluoroethylene-6 fluorinated propylene copolymer resin can be used. As the heat resistant resin, at least one resin selected from the group consisting of a polyimide resin, polyamideimide resin, polyether sulfone resin, and polyphenyl sulfone resin can be used.

A coloring pigment, rust preventive pigment, filler, and the like are added to the primer as required. A primer layer with a coating thickness of 220  $\mu\text{m}$  is applied to a steel plate surface. The primer is a fluororesin dispersion/heat resistant resin dissolution-type paint including a fluororesin insoluble in solvents. The primer is thus a thixotropic paint which is relatively difficult to roll-coat. Therefore, it is desirable the primer be roll-coated onto a steel plate by a top feed-type full reverse method.

Press-adhesion and lamination of the

tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film coated on the steel plate as a primer coating can be performed immediately after the application and baking of the primer. Alternatively, after the application and drying at about 200, the primer may be once cooled to room temperature before melting the heat resistant resin.

The tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film is pressured onto a steel plate at any temperature above the melting point of the tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film. The coating is then reheated immediately after lamination or after having been once cooled to room temperature. A common catenary-type hot blast stove, floater-type hot blast stove, electromagnetic induction heating furnace, or the like may be used for reheating. After reheating, the resin film coated steel plate may be roll-pressed prior to cooling. Cooling may be performed either by way of rapid quenching such as water-cooling or by way of slow cooling. In addition, reheating may be carried out intermittently.

The polytetrafluoroethylene resin, which most predominantly possesses the features of fluororesins, not only exhibits the highest heat resistance, chemical resistance, and radiofrequency characteristics among various thermoplastic resins, but also has a uniquely low coefficient of friction and non-stick properties.

However, because the polytetrafluoroethylene resin

does not become fluid at temperatures above the melting point, melt fabrication is not applicable to the resin. Tetrafluoroethylene-6-fluorinated propylene copolymer resins which are adaptable to melt fabrication, while possessing as much of the favorable characteristics of polytetrafluoroethylene resins as possible, has a low melting point of about 50, which renders the resins less heat resistant.

In contrast, the tetrafluoroethylene perfluoroalkyl vinyl ether copolymer resin is not only adaptable to melt fabrication, but also has a melting point of about 302310. In addition, the continuous use temperature of the resin is as high as 260. Moreover, its characteristics such as high chemical resistance, low friction, and non-stick properties are comparative to those of polytetrafluoroethylene resins. The resin can also exhibit superior design printing capabilities. Therefore, this is a fluorine-containing resin which is ideal for use in film coated steel plates requiring high heat resistance, non-stick properties, and design printing.

Any films of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer can be used without specific limitations inasmuch as the films do not have pinholes. The films having a thickness of 20 to 100  $\mu\text{m}$  are preferable. As required, the films with a color pigment incorporated therein to provide the films with a color or the films with pattern printing provided on a press-

adhesion surface using a printing ink comprising a heat resistant ink and a heat resistant printing ink binder can be used. As the heat resistant printing ink binder, a tetrafluoroethylene perfluoroalkyl vinyl ether copolymer resin, polytetrafluoroethylene resin, and the like can be given. In addition, to increase adhesive properties to the primer, the primer side surface of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film can be treated with corona discharge. The reheating temperature can be decreased by irradiating electron beams from a resin film side prior to reheating, whereby a decrease in the heat resistant non-stick properties can be prevented. As electron beams, the use of those commonly called low-energy type electron beams of less than 300 kcV is sufficient. Other electron beams and  $\gamma$ -rays can also be used. The dose of irradiation of electron beams is adjusted in the range of 550 kGy.

[Actions]

Superior anti-food burning properties are required for fluororesin film coated plates used for cookware, heat-cooking utensils, and the like. The anti-food burning properties are judged by the heat resistant non-stick properties and heat resistant adhesive properties. The heat resistant non-stick properties are evaluated, for instance, as follows. Specifically, a mixture of soy sauce, sugar, and egg in a ratio of 1:1:1, and cow's milk are dropped about 0.5 ml onto the surface of a fluororesin

film, the film is placed in an heating oven at 260 for one hour, and then cooled sufficiently, to observe if the 1:1:1 mixture of soy sauce, sugar, and egg and the cow's milk can be easily removed from the film surface without burning. The heat resistant adhesive properties are the capability to prevent formation of swells between the primer which is a mixture of a fluororesin and a heat resistant resin and the fluororesin film during the test for evaluation of the anti-food burning properties. Then, the anti-food burning properties are evaluated as the capability of satisfying both the heat resistant non-stick properties and heat resistant adhesive properties when the above test comprising dropping of the 1:1:1 mixture of soy sauce, sugar, and egg and the cow's milk, heating at 260 for one hour, and cooling has been repeated twenty times.

The heat resistant adhesive properties are improved by maintaining a high reheating temperature. For example, although the adhesive properties of a fluororesin film for the primer is insufficient before reheating in practical use, this can be increased to a level adaptable to application by reheating. Moreover, a high reheating temperature can not only increase the heat resistant adhesive properties, but also is effective in shortening the reheating time. However, the heat resistant non-stick properties decrease markedly when the reheating temperature is raised. The present inventors have conducted extensive studies related to the phenomenon of a decrease in the heat

resistant non-stick properties accompanied by a reheating temperature rise. As a result, the inventors have found that when a film of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer (which is inherently heat resistant resin) is heated, oxygen present in the vicinity of the film surface during the reheating operation oxidizes the film, even if the heating temperature is as low as a temperature at which no heat resistant problems occur with bulk resins. The surface oxidation increases the affinity of the film with the above-mentioned mixed liquid and cow's milk, which results in a decrease in the heat resistant non-stick properties. The surface oxidation of the film is explained by a decrease in the contact angle with water on the film surface according to a reheating temperature rise and a decrease in the fluorine atom concentration and increase in the oxygen atom concentration in the outermost layer as determined by a photoelectron spectroscopic analysis of the film surface. Specifically, while the heat resistant adhesive properties relate to the characteristics in the interface of a resin film and a primer, the heat resistant non-stick properties are the characteristics in the outermost layer a resin film.

For these reasons, to secure sufficient heat resistant adhesive properties and heat resistant non-stick properties, electron beams are irradiated at a dose of 550 kGy in the present invention. By irradiation of electron beams, the molecule chain of the fluororesins which are the

component of the tetrafluoroethylene perfluoroalkyl vinyl ether copolymer forming the film and the primer is cut, thereby decreasing the molecular weight. This decreases the melt viscosity, rendering the fluororesins which are present on the primer surface easily melted and diffused during reheating. Consequently, superior heat resistant adhesive properties are exhibited by reheating at a low temperature. However, to ensure sufficient heat resistant adhesive properties, the steel plates should be heated at temperature of 320 or higher. On the other hand, surface oxidation of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film becomes remarkable according to the increase in the reheating temperature, which significantly impairs the heat resistant non-stick properties.

The molecular chains cut by irradiation of electron beams are easy to move, so that the molecules near the film surface in which the molecular chains have been oxidized tend to have lower energy and are thermodynamically stable. These molecules easily penetrate deep into the film and, instead, non-oxidized molecules move upward during reheating. As a result, oxidation during reheating is suppressed, affording the steel plate with superior heat resistant non-stick properties. Moreover, since the reheating temperature can be lowered, it is possible to produce products with superior properties by reheating at a temperature lower than 400. To ensure such an effect by irradiation of electron beams, it is necessary to adjust

the dose of electron beams in the range of 550 kGy. If less than 5 kGy, the heat resistant adhesive properties will be insufficient due to inadequate cutting of molecular chains, making it difficult for the oxidized parts on the film surface to penetrate deep into the film. On the other hand, if irradiation exceeds 50 kGy, the molecular chain cut may become excessive, resulting in formation of cracks on the film surface during reheating. This may allow the mixed liquid and the like to physically invade the coated surface during the test for anti-food burning properties.

[Examples]

A 430SS stainless steel plate with a thickness 0.45 mm was degreased and subjected to a coating-type chromate treatment. Then, a mixed resin consisting of a polytetrafluoroethylene resin and a polyether sulfone resin was applied to a thickness of 7  $\mu\text{m}$ , followed by baking at 400. A film of transparent tetrafluoroethylene perfluoroalkyl vinyl ether copolymer with a thickness 40  $\mu\text{m}$  was pressed and laminated at a steel plate temperature of 380, followed by cooling with water. Next, after irradiation of electron beams under the conditions shown in Table 1, the film was reheated at the steel plate temperature shown in Table 1, instantly followed by cooling with water. The heat resistant adhesive properties, heat resistant non-stick properties, contact angle with water on the resin film surface after grinding, and O/F atomic ratio by photoelectron spectroscopic analysis of the resulting

resin film coated steel plate are shown in Table 1.

Table 1 The effect of the reheating temperature and electron beam irradiation on the anti-food-burning properties and surface characteristics

Test No.	Electron beam irradiation conditions	Steel plate temperature during reheating (°)	Anti-food-burning properties	Surface characteristics
1	10 kGy	330	Heat resistant adhesive properties	Heat resistant non-stick properties
2	10 kGy	350	20 times or more	20 times or more
3	10 kGy	380	20 times or more	20 times or more
4	30 kGy	330	20 times or more	20 times or more
5	30 kGy	350	20 times or more	20 times or more
6	30 kGy	380	One time	20 times or more
7	None	330	One time	20 times or more
8	None	350	One time	20 times or more
9	None	380	One time	One time
10	10 kGy	300	One time	One time
11	100 kGy	350	Three times	Three times

\* The reheating time was constant at 15 minutes.

\* The water contact angle for tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film was 110°.

\* The O/F atomic ratio for tetrafluoroethylene perfluoroalkyl vinyl ether copolymer film was 0.01.

\* Sample irradiated by 10 Mrad electron beams created cracks in three repetitions of the anti-food-burning properties test.

The heat resistant adhesive properties and heat resistant non-stick properties shown in Table 1 are the results obtained by the previously mentioned anti-food burning properties test. If the 1:1:1 mixture of soy sauce, sugar, and egg and the cow's milk could be removed from the film surface without burning, the sample was evaluated as "Good"; if not removed due to burning, the sample was evaluated as "Bad". In the evaluation of heat resistant adhesive properties, if no swelling was produced in the interface of the primer and resin film, the sample was rated as "Good", whereas if swelling was produced, the sample was evaluated as "Bad". The tests for the heat resistant non-stick properties and heat resistant adhesive properties were repeated for all samples until neither of the properties could be evaluated as "Good". The number of repetitions of these tests is indicated as the heat resistant non-stick properties and heat resistant adhesive property in Table 1. In the evaluation results in Table 1, it is desirable for the products to exhibit 20 times or more "Good" results in order to be applied to the manufacture of cookware or heat-cooking utensils. As can be seen in Table 1, in the Test Nos. 1-6 for which reheating was carried out after electron beam irradiation, sufficient heat resistant non-stick properties were exhibited after twenty repetitions of the tests of the anti-food-burning properties. This is presumed to be the result of increased heat resistant adhesive properties by

reheating at a low temperature after electron beam irradiation.

On the other hand, in the Comparative Examples of Test Nos. 7 and 8, in which the samples were not irradiated by electron beams, although the heat resistant non-stick properties were equivalent to the Examples of the present invention, the heat resistant adhesive properties were inferior. In the Test No. 9, both the heat resistant adhesive properties and heat resistant non-stick properties were inferior. In the Test No. 10 in which a lower reheating temperature was applied, the heat resistant adhesive properties were inferior, although the heat resistant non-stick properties were favorable. In the Test No. 11 in which electron beams were irradiated at a higher dose, although the heat resistant adhesive properties and heat resistant non-stick properties were acceptable, cracks were produced in the film. This is due to the excessively reduced molecular weight of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer by irradiation of excessive electron beams. As clear from these comparisons, a steel plate coated with a fluorine-containing resin which exhibits excellent heat resistant adhesive properties and heat resistant non-stick properties can be obtained by setting the dose of electron beams at 550 kGy and reheating the film at a temperature of 320 or more.

#### [Effect of the Invention]

As described above, in the present invention a film

of tetrafluoroethylene perfluoroalkyl vinyl ether copolymer is caused to adhere to the surface of a steel plate via a primer, and electron beams were irradiated from the film side, followed by reheating.

The reheating temperature can be lowered by irradiation of electron beams, thereby suppressing the oxidation of the film surface. This in turn prevents the heat resistant adhesive properties from becoming impaired. As a result, a steel plate coated with a fluorine-containing resin exhibits both excellent heat resistant adhesive properties and excellent heat resistant non-stick properties, and is suitable for use as a material for cookware and heat-cooking utensils.

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(54) TITLE OF THE INVENTION: RESIN TUBE

(57) Abstract:

[Object] To improve adhesiveness between a fluoro resin layer and a polyamide resin layer in order to prevent interlayer delamination of a multilayered resin tube without using a complicated surface chemical treatment.

[Constitution] A resin tube comprising at least an inner layer and an outer layer, wherein the inner layer is formed from a fluoro resin and the outer layer is formed from a polyamide resin, and a crosslinking structure is introduced between the polymer molecules of the inner layer and the outer layer by irradiation.

[Claims]

[Claim 1]

A resin tube comprising at least an inner layer and an outer layer, wherein the inner layer is formed from a fluoro resin and the outer layer is formed from a polyamide resin, and a crosslinking structure is introduced between the polymer molecules of the inner layer and the outer layer by irradiation.

[Detailed Description of the Invention]

[Technical field]

The present invention relates to a resin tube useful as fuel piping for automobiles and the like. In particular, the present invention relates to a resin tube comprising a laminated layer consisting of a fluoro resin layer and a polyamide resin layer.

[Background Technology]

Up to now, various materials have been used as tubes for piping such as tubes used for automobiles. For example, metals, resins, and the like are used in tubes for fuel piping or in connections. However, since metal tubes not only rust but also are extremely heavy, such tubes cannot meet the demand for lightweight automobiles. Therefore, resin tubes that are light in weight and do not rust, such as one made of a polyamide resin, have been widely used in recent years.

However, a single layer tube made of a polyamide resin allows a large amount of gasoline to permeate,

thereby causing environmental pollution. Because of this, in order to reduce the amount of gasoline permeated, tubes having a two-layered structure comprising a fluoro resin layer having excellent gasoline-barrier characteristics provided inside the polyamide resin layer has been considered. However, because the adhesiveness of a fluoro resin and a polyamide resin is low, such tubes may be clogged during use due to the delamination of the layers.

This problem can be overcome by providing the surface of the fluoro resin layer with a chemical treatment to introduce an active group. In this chemical treatment, the fluoro resin inner layer is molded by extrusion molding. An active group is introduced by immersing the molded layer in a chemical treatment solution containing a sodium-ammonia complex or a sodium-naphthalene complex. The surface of the inner layer is then washed and dried. The outer layer is subsequently laminated on the inner layer using a polyamide resin. Therefore, the manufacturing process becomes very complicated and quality control becomes difficult due to the overseeing of the treatment when using a chemical solution, the degree of washing of the surface of the tube, and the like.

[Problems to be Solved by the Invention]

The present invention has been achieved in view of the above situation. An object of the present invention is to provide a resin tube having a multilayered structure

while exhibiting no interlayer delamination by improving the adhesiveness of the fluoro resin layer and the polyamide resin layer without using a complicated surface chemical treatment.

[Means for the Solution of the Problems]

According to the present invention, the above object can be achieved by a resin tube comprising at least an inner layer and an outer layer, wherein the inner layer is formed from a fluoro resin and the outer layer is formed from a polyamide resin, and a crosslinking structure is introduced between the polymer molecules of the inner layer and the outer layer by irradiation.

[Constitution]

According to the resin tube of the present invention, there are no specific limitations to the fluoro resin for the inner layer and the polyamide resin for the outer layer. Any polymer in which a crosslinking structure is introduced by radiation can be used.

As examples of the fluoro resin, polyvinylidenefluoride (PVDF), polychlorotrifluoroethylene (CTFE), copolymers such as a copolymer of ethylene and tetrafluoroethylene (ETFE) and a copolymer of ethylene and polychlorotrifluoroethylene (ECTFE), graft polymers, and polymer blends can be used.

As examples of the polyamide resin, conventionally known aliphatic or aromatic polymers such as polymers of lactam, condensation polymers of diamine and dicarboxylic

acid, polymers of amino acid, copolymers of these compounds, and polymer blends of these polymers can be used appropriately. Specific examples of the polyamide resin include Nylon 6, Nylon 66, Nylon 610, Nylon 612, Nylon 11, Nylon 12 and the like.

Crosslinking improvers are added to these resin materials in order to improve crosslinking efficiency, as required. Examples of well-known crosslinking improvers include HDDA (hexanediol diacrylate), TPGDA (tripropylene glycol diacrylate), DEGDA (diethylene glycol diacrylate), TEGDA (tetraethylene glycol diacrylate), TMPTA (trimethylolpropane triacrylate), GPTA (glycerolpropoxy triacrylate), TMPEOTA (trimethylolpropaneethoxy triacrylate), PETA (pentaerythritol acrylate), TAIC (triallyl isocyanurate), THEICA (trishydroxyethylisocyanuric acrylate),  $\text{SnCl}_2$ , and the like. Any of these crosslinking improvers can be used in the present invention. Types and amounts of crosslinking improvers to be used are determined according to the types of the resin materials and the desired degree of a crosslinking structure. In addition, other characteristic giving agents or additives can be added to the resin materials.

In the present invention, each of the fluoro resin and the polyamide resin is homogeneously mixed at a temperature lower than the melting point of the resins. According to a conventional operation of extrusion

molding, the inner and outer layers are respectively molded from the fluoro resin and the polyamide resin using a two-axle screw extruder and the like to form the resin tube having a lamination structure. For example, a tube having a two-layered structure is prepared by simultaneously molding the inner and outer layers on a mandrel by extrusion molding and curing or solidifying the tube to form a tube having a predetermined inner diameter. This molding can be performed without using a mandrel. The thickness of the tube is appropriately determined depending on the purpose. For example, in the case of the tube for fuel piping for automobiles, the thickness of the inner layer and the outer layer is preferably 0.3 mm and 0.7 mm, respectively.

In the present invention, the fluoro resin for the inner layer and the polyamide resin for the outer layer are subsequently crosslinked by exposure to radiation. In particular, adhesiveness of these layers can be effectively improved by introducing a crosslinking structure between polymer molecules of the inner and outer layers. As radiation to be used, electromagnetic waves such as electron beams, -rays, and -rays are usually employed. The dose is properly determined depending on types of the resin materials or crosslinking improvers, desired adhesive strength, and the like. As described above, according to the present invention, since the adhesiveness of the layers is improved by the irradiation,

the process and quality control become remarkably simple compared to the conventional method using a surface chemical treatment. Because of this, the tube can be manufactured with superior productivity.

According to the present invention, a protective layer having a thickness of 0.5-2 mm may be provided on the outer surface of the resin tube using solid materials such as rubber, flexible resins, and thermoplastic elastomers, foam, and the like. In this case, such a protective layer can be made to adhere to the resin tube without using adhesives by irradiating the resin tube after laminating the protective layer on the resin tube.

#### [Examples]

The present invention will now be described in more detail by way of examples below, which should not be construed as limiting the present invention. It should be clearly understood that numerous modifications, amendments, and variations of the present invention other than the following Examples and as specifically described herein are possible on the basis of the knowledge of a person who is skilled in the art.

According to a conventional extrusion molding process, four tubes for Examples and two tubes for Comparative Examples having a two-layered structure as shown in Table 1 were formed. The inner and outer diameters of the tubes were 6 mm and 8 mm, respectively. The thickness of the inner and outer layers was 0.3 mm and

7 mm, respectively. In the examples, a crosslinking structure was introduced into the tubes by exposure to radiation (electron beams). In Comparative Example 1, the outer layer was laminated after providing the inner layer with surface chemical treatment. The tube in Comparative Example 2 was provided with neither exposure to radiation nor surface chemical treatment.

Test specimens having a width of 1 inch were collected from each tube. Peel strength of the test specimens was measured according to the 180 degree friction test of JIS-K-6301. The results are shown in Table 1. Symbols in Table 1 are as follows.

ETFE: copolymer of ethylene and tetrafluoroethylene

F-1: flexible fluoro resin (trade name: Cefralsoft G180, manufactured by Central Glass Co., Ltd.)

F-2: polymer blend of F-1 and polyvinylidenefluoride in a ratio (weight ratio) of 50:100

TAIC: triallylisocyanurate

PA12p: Nylon 12 blended with plasticizers

[Table 1]

			Example				Comparative Example	
Tube structure	Inner layer	Fluoro resin	1	2	3	4	1	2
		Crosslinking improver	TAIC	TAIC	TAIC	TAIC	-	-
		wt%	5	5	5	5	-	-
	Outer layer	Polyamide resin	PA12p	PA12p	PA12p	PA12p	PA12p	PA12p
		Crosslinking improver	TAIC	TAIC	TAIC	TAIC	-	-
		wt%	5	5	5	5	-	-
Exposure to radiation							(*)	

Dose (Mrad)	10	10	10	20	-	-
Peel strength (kgf/inch)	2.9	3.3	3.0	3.6	3.2	0.1

(\*) The inner layer was provided with a surface chemical treatment.

As is clear from the results in Table 1, the tube in Comparative Example 2, in which the inner layer was only laminated on the outer layer without any treatment, exhibited low peel strength and may experience delamination. The tube in Comparative Example 1 exhibited improved peel strength because of the surface chemical treatment, however, the manufacturing process became complicated. On the other hand, peel strength of the tubes in Examples 1-4 was effectively improved only after exposure to radiation.

#### [Effect of the Invention]

As is clear from the above description, according to the resin tube of the present invention, since a crosslinking structure is introduced between polymer molecules of the inner layer and the outer layer by irradiation, adhesiveness of the inner layer formed from a fluoro resin and the outer layer formed from a polyamide resin is effectively improved, thereby advantageously preventing interlayer delamination. Since the irradiation process is more simple compared to a conventional surface chemical treatment and quality control is easy, the resin tube can be manufactured with extremely high productivity.

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(54)【発明の名称】 フッ素含有樹脂フィルム被覆鋼板の製造方法

(57)【要約】

【課題】 耐熱接着性及び耐熱非粘着性の双方に優れ、  
食品調理器具、加熱調理器具等として好適な樹脂フィル  
ム被覆鋼板を得る。

【解決手段】 フッ素樹脂と耐熱性樹脂との混合樹脂か  
らなるプライマーを鋼板表面に塗布し焼き付けた後、鋼  
板を予熱し、4フッ化エチレンバーフルオロアルキルビ  
ニルエーテル共重合体フィルムを圧着・積層し、フィル  
ム面側から線量5～50kGyで電子線を照射し、次い  
で板温320℃以上に鋼板を再加熱する。

## 【特許請求の範囲】

【請求項1】 フッ素樹脂と耐熱性樹脂との混合樹脂からなるプライマーを鋼板表面に塗布し焼き付けた後、鋼板を予熱し、4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムを圧着・積層し、樹脂フィルム面側から線量5～50kGyの電子線を照射し、次いで鋼板を板温320℃以上に再加熱するフッ素含有樹脂フィルム被覆鋼板の製造方法。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、食品調理用器具、加熱調理用器具等の厨房製品に好適なフッ素樹脂フィルム被覆鋼板を製造する方法に関する。

## 【0002】

【従来の技術】フッ素樹脂は、優れた耐熱性、非粘着性、耐汚染性等を活用し、鋼材との複合材としてパン、ケーキの焼き型、フライパン等の食品調理器具、電子レンジ内板、ジャー内釜、ガステーブル天板等の加熱調理器具に広く使用されている。従来の食品調理器具、加熱調理器具等では、何れもフッ素樹脂又はフッ素樹脂と耐熱性樹脂との混合樹脂を鋼板表面に塗布し、高温焼成することによりフッ素樹脂皮膜を形成している。しかし、フッ素系塗料の焼付けによって形成されることから、塗布、焼付け工程でピンホールの発生を皆無とすることが困難である。そのため、非粘着性、耐汚染性を長期間にわたって維持することができず、またピンホールを介して各種の欠陥が発生することもある。

【0003】ピンホールは、無孔質のフッ素樹脂フィルムで鋼板表面を被覆することにより防止される。たとえば、特開昭52-124081号公報、特開昭53-98372号公報では、フッ素含有重合体の融点以上の温度に加熱した鋼板表面にフッ素含有重合体の無孔質フィルムを積層し、ゴムロールによる押圧で無孔質フィルムを鋼板に貼り付けている。特開平5-162243号公報では、フッ素樹脂と耐熱樹脂との混合樹脂による下地処理層を介し熱可塑性フッ素樹脂フィルムを鋼板表面に熱融着している。また、特開平6-344505号公報、特開平7-125136号公報では、加熱及び再加熱の温度条件を調整することによりフッ素樹脂フィルムの密着性を改善している。

## 【0004】

【発明が解決しようとする課題】しかし、従来の製造条件では、耐熱非粘着性及び耐熱接着性を共に満足するフッ素樹脂フィルム被覆鋼板を得ることが困難である。特に食品調理器具、食品加熱器具等の用途では耐食品焦げ付き性に優れていることが要求されるが、従来のフッ素樹脂フィルム被覆鋼板では十分な耐食品焦げ付き性が得られない。本発明は、このような問題を解消すべく案出されたものであり、鋼板に貼り付けたフッ素含有樹脂フィルムにフィルム面側から電子線を照射することによ

り、耐焦げ付き性を改善したフッ素含有樹脂フィルム被覆鋼板を製造することを目的とする。

## 【0005】

【課題を解決するための手段】本発明のフッ素含有樹脂フィルム被覆鋼板製造方法は、その目的を達成するため、フッ素樹脂と耐熱性樹脂との混合樹脂からなるプライマーを鋼板表面に塗布し焼き付けた後、鋼板を予熱し、4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムを圧着・積層し、樹脂フィルム面側から線量5～50kGyの電子線を照射し、次いで鋼板を板温320℃以上に再加熱することを特徴とする。使用される鋼板は、必要に応じて磷酸塩処理、塗布型クロメート処理等を施した55%A1-Zn合金めっき鋼板、A1めっき鋼板、ステンレス鋼板等がある。4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムの圧着・積層に先立って、フッ素樹脂と耐熱性樹脂の混合樹脂からなるプライマーを鋼板に塗布、焼付けする。

【0006】プライマーの成分であるフッ素樹脂としては、ポリ4フッ化エチレン樹脂、4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体樹脂、4フッ化エチレン-6フッ化プロピレン共重合体樹脂から選ばれた少なくとも一つの樹脂が使用される。耐熱性樹脂としては、ポリイミド樹脂、ポリアミドイミド樹脂、ポリエーテルサルファン樹脂、ポリフェニルサルファン樹脂から選ばれた少なくとも一つの樹脂が使用される。プライマーには、必要に応じて着色顔料、防錆顔料、体质顔料等が添加される。プライマー層は、乾燥塗膜厚さが2～20μmとなるように鋼板表面に塗布される。プライマーは、溶剤に溶解しないフッ素樹脂を含むフッ素樹脂分散／耐熱性樹脂溶解型塗料であることから、チクソトロピックな塗料であり、ロールコート性に比較的乏しい。そのため、トップフィード型でフルリバース法によるロールコートでプライマーを鋼板に塗布することが好みしい。

【0007】プライマー塗装した鋼板に対する4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムの圧着・積層は、プライマーの塗装、焼付け後、直ちに行うことができる。また、プライマーを塗布し、200℃前後で乾燥させた後、耐熱性樹脂が溶融しない段階で一旦室温まで冷却しても良い。4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムを圧着する際の鋼板温度は、4フッ化エチレンパーカルオロアルキルビニルエーテル共重合体フィルムの融点以上であれば良い。積層後、直ちに再加熱し、或いは一旦室温まで冷却した後で再加熱する。再加熱には、一般的なカタナリ式熱風炉、フロータ式熱風炉、電磁誘導加熱炉等が使用される。また、再加熱後の冷却に先立って、樹脂フィルム被覆鋼板をロール加圧しても良い。冷却は、水冷等の急冷、或いは徐冷の何れでもよい。ま

た、再加熱では、再加熱時間を分割することもできる。

【0008】フッ素樹脂の特徴を最大にしているポリ4フッ化エチレン樹脂は、熱可塑性樹脂の中では最高の耐熱性、耐薬品性、高周波特性を示し、特異な低摩擦係数及び非粘着性を備えている。しかし、融点以上になつても流動しないため、溶融成形できない。ポリ4フッ化エチレン樹脂の特性をできるだけ保持し、溶融成形を可能にした4フッ化エチレン-6フッ化プロピレン共重合体樹脂は、融点が約50°Cと低いため、耐熱性に劣る。これに対し、4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体樹脂は、溶融成形可能な上に融点が302~310°Cと高く、連続使用温度も260°Cと高い。しかも、耐薬品性、低摩擦性、非粘着性等の性質がポリ4フッ化エチレン樹脂に比較して遜色なく、フィルムの印刷意匠性も優れている。したがって、耐熱性、非粘着性及び意匠印刷性が要求されるフィルム被覆鋼板に最も適したフッ素系樹脂である。

【0009】4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体フィルムとしては、ピンホールがないものが使用され、特に限定されるものではないが20~100μmの厚みをもつフィルムが好ましい。また、必要に応じて着色のために耐熱型の着色顔料を配合したものや、耐熱型インクと耐熱性印刷インクバインダーからなる印刷インクを使用して柄印刷をプライマーとの圧着面に施したもののが使用される。耐熱性印刷インクバインダーには、4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体樹脂、ポリ4フッ化エチレン樹脂等がある。更に、プライマーに対する接着性を高めるため、4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体フィルムのプライマー側表面をコロナ放電処理することもできる。再加熱に先立って電子線を樹脂フィルム面側から照射することにより、再加熱温度を低下することができ、耐熱非粘着性の低下が抑えられる。照射電子線は、一般に低エネルギー型と呼ばれている300kV未満の電子線で十分であるが、それ以外の電子線やγ線も使用できる。照射電子線の線量は、5~50kGyの範囲に調整される。

#### 【0010】

【作用】食品調理器具、加熱調理器具等に使用されるフッ素樹脂フィルム被覆鋼板としては、耐食品焦げ付き性に優れていることが要求される。耐食品焦げ付き性は、耐熱非粘着性及び耐熱接着性で判定される。耐熱非粘着性は、たとえば醤油：砂糖：卵=1:1:1の混合液及び牛乳をフッ素樹脂フィルムの表面に0.5ml程度滴下し、これを260°Cの加熱炉に1時間入れ、十分冷却した後、醤油：砂糖：卵=1:1:1の混合液及び牛乳がフッ素樹脂フィルムに焦げ付くことなく容易に除去できるか否かで評価される。また、この耐食品焦げ付き性試験時にフッ素樹脂と耐熱樹脂との混合樹脂からなるプライマーとフッ素樹脂フィルムとの間にフクレが発生し

ない十分な耐熱接着性が要求される。更に、耐焦げ付き性に関しては、醤油：砂糖：卵=1:1:1の混合液及び牛乳を滴下し、260°C×1時間加熱、冷却を20サイクルを程度繰り返しても、耐熱非粘着性及び耐熱接着性が保持されていることが望まれる。

【0011】耐熱接着性は、再加熱温度を高く設定することにより改善される。たとえば、プライマーに対するフッ素樹脂フィルムの接着性は、再加熱前では実用上不十分であるが、再加熱によって用途に応じたレベルまで向上させることができる。また、高い再加熱温度は、十分な耐熱接着性を発現させると共に、再加熱時間を短縮する上でも有効である。しかし、耐熱非粘着性は、再加熱温度の上昇に伴つて著しく低下する。本発明者等は、再加熱温度の上昇に伴つて耐熱非粘着性が低下する現象を種々調査・研究した。耐熱樹脂である4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体フィルムでは、特にバルクでの耐熱性に関しては問題とならないような温度での加熱でも、再加熱時にフィルム表面附近に存在する酸素がフィルム表面を酸化させることを見い出した。表面酸化は、前述した混合液や牛乳に対してフィルム表面を馴染みやすくし、結果として耐熱非粘着性を低下させる原因になる。フィルムの表面酸化は、再加熱温度の上昇に従つてフィルム表面の耐水接触角が減少し、またフィルム表面の光電子分光分析の結果として極表層におけるF原子濃度の減少及びO原子濃度の増加から説明できる。すなわち、耐熱接着性は樹脂フィルムとプライマーとの界面特性であるのに対し、耐熱非粘着性は樹脂フィルム極表層の特性である。

【0012】このようなことから、本発明においては、十分な耐熱接着性及び耐熱非粘着性を確保するために、線量5~50kGyで電子線を照射するように設定した。電子線照射によって、フィルムを形成している4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体及びプライマーの成分であるフッ素樹脂の分子鎖が分断され、分子量が小さくなる。その結果、溶融粘度が低下し、再加熱時にプライマー表面に存在するフッ素樹脂との間での溶融拡散が起り易くなる。そのため、低温の再加熱でも、優れた耐熱接着性が発現する。ただし、十分な耐熱接着性を得るためにには、320°C以上の鋼板温度が必要である。一方、再加熱温度の上昇に伴つて、4フッ化エチレン-パーカルオロアルキルビニルエーテル共重合体フィルムの表面酸化が著しくなり、耐熱非粘着性が大きく低下する。

【0013】この点、電子線照射によって分断された分子鎖は、動き易くなっている。そのため、フィルム表層部に位置する分子鎖の酸化された部位は、熱力学的に安定な低エネルギー面になり易く、すなわちフィルム内部に潜り込み易くなり、代わって非酸化部位が再加熱下に刻々と表面移行、形成するようになる。その結果、再加熱時の酸化が抑制され、優れた耐熱非粘着性が得られ

る。また、再加熱温度を低下できることから、高温での再加熱が必要なくなり、400°C未満の再加熱温度で十分な特性を発現できる。電子線照射によってこのような作用を効果的に得るためにには、線量を5~50kGyの範囲に調整することが必要である。5kGyに満たない線量では、分子鎖の分断が少ないために耐熱接着性が低く、フィルム表層部の酸化部位も潜り込みにくくなる。逆に、50kGyを超える線量では、分子鎖が過剰に分断され、再加熱時にフィルム表面にクラックが発生し、耐食品焦げ付き性試験で混合液等が物理的に侵入し易くなる。

## 【0014】

【実施例】板厚0.45mmのSUS430ステンレス鋼板を脱脂し、塗布型クロメート処理を施し、ポリ4フッ化エチレン樹脂/ポリエーテルサルファン樹脂からなる混合樹脂を乾燥膜厚7μmで塗布し、400°Cで焼き付けた。そして、厚さ40μmの透明4フッ化エチレン/パーカルオロアルキルビニルエーテル共重合体フィルムを、鋼板温度380°Cで圧着するように調整し、積層し、水冷した。次いで、表1に示す条件下で電子線を照射した後、表1に示す鋼板温度に再加熱し、直ちに水冷した。得られた樹脂フィルム被覆鋼板の耐熱接着性、耐熱非粘着性、研磨後の樹脂フィルム面の耐水接触角及び光電子分光分析に基づくO/F原子比を表1に併せて示す。

【0015】表1に示した耐熱接着性及び耐熱非粘着性は、前述した耐食品焦げ付き試験によって得られた値であり、醤油:砂糖:卵=1:1:1混合液及び牛乳が樹脂フィルム面に焦げ付くことなく除去できる場合を耐熱非粘着性が「優」であり、焦げ付いて取れない場合を

「劣」として評価し、プライマーと樹脂フィルムとの間にフクレが発生しない場合を耐熱接着性が「優」であり、フクレが発生した場合を「劣」として評価した。そして、耐熱非粘着性及び耐熱接着性の何れも「優」の試験片について、それぞれの特性が「優」でなくなるまで同じ試験を繰り返した。表1では、この繰り返し回数で耐熱接着性及び耐熱非粘着性を表している。なお、食品調理器具、加熱調理器具等の用途では、「優」が維持される繰り返し回数が20回以上であることが好ましい。表1にみられるように、電子線照射後に再加熱した試験番号1~6では、耐食品焦げ付き試験を20回以上繰り返した後でも十分な耐熱非粘着性を呈していた。これは、電子線照射により、低温での再加熱で耐熱接着性が上昇した結果であると推察される。

【0016】他方、電子線照射をしない試験番号7, 8では、本発明例と同等な耐熱非粘着性を呈しているものの、耐熱接着性が劣っていた。同じく試験番号9では、耐熱接着性及び耐熱非粘着性の双方とも劣っていた。また、再加熱温度を低く設定した試験番号10では、耐熱非粘着性が良好であるものの、耐熱接着性が劣っていた。電子線量を高く設定した試験番号11では、耐熱接着性及び耐熱非粘着性共に良好であるが、電子線照射によって4フッ化エチレン/パーカルオロアルキルビニルエーテル共重合体の分子量が小さくなりすぎ、フィルムにクラックが発生した。この対比から明らかなように、電子線量を5~50kGyに設定し、320°C以上で再加熱することにより、耐熱接着性及び耐熱非粘着性の双方に優れたフッ素含有樹脂フィルム被覆鋼板が得られることが確認される。

## 【0017】

表1：再加熱及び電子線照射が耐食品焦げ付き性及び表面特性に及ぼす影響

試験番号	電子線の照射条件	再加熱時の鋼板温度(°C)	耐食品焦げ付き性		表面特性		区分
			耐熱接着性	耐熱非粘着性	耐水接触角(度)	O/F原子比	
1	10kGy	330	20回以上	20回以上	110	0.01	本発明例
2	10kGy	350	20回以上	20回以上	110	0.01	
3	10kGy	380	20回以上	20回以上	109	0.01	
4	30kGy	330	20回以上	20回以上	110	0.01	
5	30kGy	350	20回以上	20回以上	110	0.01	
6	30kGy	380	20回以上	20回以上	109	0.01	
7	照射なし	330	1回	20回以上	110	0.01	比較例
8	照射なし	350	1回	20回以上	109	0.01	
9	照射なし	380	1回	1回	102	0.04	
10	10kGy	300	1回	1回	110	0.01	
11	100kGy	350	3回	3回	109	0.01	

再加熱時間は16分間で一定

耐水接触角は、4フッ化エチレン/パーカルオロアルキルビニルエーテル共重合体フィルムでは110度

O/F原子比は、4フッ化エチレン/パーカルオロアルキルビニルエーテル共重合体フィルムでは0.01

10Mradの電子線を照射したものは、3回でクラック発生

## 【0018】

【発明の効果】以上に説明したように、本発明において

は、プライマーを介して4フッ化エチレンバーフルオロアルキルビニルエーテル共重合体フィルムを鋼板表面に貼り付け、フィルム面側から電子線を照射した後、再加熱している。電子線照射によって再加熱温度を下げることができ、フィルム表層の酸化が抑制され、ひいては耐

熱非粘着性の低下が防止される。その結果、耐熱接着性及び耐熱非粘着性の双方に優れ、食品調理器具、加熱調理器具等として好適な樹脂フィルム被覆鋼板が得られる。

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フロントページの続き

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